



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants : T. Kanda et al  
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For : GAS-BARRIER MULTI-LAYER STRUCTURE  
Art Unit & Examiner : 1711, T. Thaot

DECLARATION UNDER 37 CFR 1.132

Honorable Commissioner of Patents and Trademarks,  
Washington, D.C. 20231

Sir:

I, Tomomichi Kanda, of c/o Mitsubishi Gas Chemical Company, Inc., Hiratsuka Research Laboratory, 6-2, Higashiyawata 5-chome, Hiratsuka-shi, Kanagawa, Japan, declare that:

1. I entered Mitsubishi Gas Chemical Company, Inc., in April 1997, and was then assigned to the Hiratsuka Research Laboratory. I have engaged in the research and development of polymer products.

2. I am one of the named inventors of the above-identified application, and understand the English language.

3. Purpose of experiment.

The feature of the present Application lies in a polyamide resin prepared by a polycondensation method comprising the steps of a melt-polymerization and a solid-phase polymerization. The polyamide resin of the present Application provides superior effect in both the formability of multi-layer sheet and the formability of multi-layer container, compared with the polyamide resin of Matlack reference (US Pat. 5,028,462) prepared by a polycondensation method without a solid-phase polymerization.

For the purpose of proving the above fact, the following experiments were conducted.

#### 4. Experimental Method and Results

##### 4-1) Production of Polyamide Resins

Polyamide 1 (Example 2 in the present specification).

The procedure of Example 2 was repeated except that a dicarboxylic acid component composed of 94 mol% of adipic acid and 6 mol% of isophthalic acid was used and a reaction temperature of 255 to 260°C for melt-polymerization was adopted, thereby obtaining a polyamide having a relative viscosity of 2.1 and a melting point of 232 °C.

Next, the polyamide thus obtained was subjected to solid polymerization at a reaction temperature of 140 to 180°C and under a pressure of 1 torr or lower in the reaction system to

produce Polyamide 1 having a relative viscosity of 2.5, a melting point of 232 °C, and a glass transition temperature (Tg) of 92 °C. A single-layer non-stretched film extruded from Polyamide 1 showed a half crystallization time of 62 sec. and an oxygen transmission coefficient of 0.07 cc.mm/m<sup>2</sup>.day.atm.

Polyamide 2 (Example 3 in the present specification).

The same procedure in Example 3 was repeated except that a dicarboxylic acid component composed of 85 mol% of adipic acid and 15 mol% of isophthalic acid was used, and other conditions in the melt- or solid-polymerization were the same as in Polyamide 1, thereby producing Polyamide 2 having a relative viscosity of 2.5, a melting point of 216°C, and Tg of 98°C.

A half crystallization time was 455 sec. and an oxygen transmission coefficient was 0.07 cc.mm/m<sup>2</sup>.day.atm.

Polyamide 3 (Comparative Example 1 in the present specification).

The same procedure in Comparative Example 1 was repeated except that 100 mol% of an adipic acid was used, and other conditions in the melt- or solid-polymerization were the same as in Polyamide 1, thereby producing Polyamide 3 having a relative viscosity of 2.6, a melting point of 240°C, and Tg of 88°C. A half crystallization time was 25 sec. and an oxygen transmission coefficient was 0.09 cc.mm/m<sup>2</sup>.day.atm.

Polyamide 4 (Example 3 in Matlack reference, at line 2 in Table).

Polyamide 4 was produced by melt-polymerization of metaxylenediamine and a dicarboxylic acid component of 85 mol% of adipic acid and 15 mol% of isophthalic acid, in the manner described in Example 3 of Matlack reference. Thus obtained Polyamide 4 had a relative viscosity of 2.0, a melting point of 215°C, and Tg of 97°C. A half crystallization time and an oxygen transmission coefficient of a single-layer non-stretched film extruded from Polyamide 4 were 403 sec. and 0.08 cc.mm/m<sup>2</sup>.day.atm.

Polyamide 5 (Example 3 in Matlack reference, at line 2 in Table).

The same procedure in Polyamide 4 was repeated except that a feeding molar ratio of an adipic acid /an isophthalic acid was set up at 93/7, thereby conducting polymerization of Polyamide 5. Polyamide 5 thus obtained had a relative viscosity of 2.0, a melting point of 230 °C, and Tg of 92°C. A half crystallization time and an oxygen transmission coefficient of a single-layer non-stretched film extruded from Polyamide 5 were 52 sec. and 0.07 cc.mm/m<sup>2</sup>.day.atm.

#### 4-2) Evaluation-method for Physical Properties.

In accordance with the various kinds of methods described at the beginning of Examples in the Specification, (1) Relative Viscosity, (2) Half Crystallization Time, (3) Melting Point, and (4) Oxygen Transmission Coefficient were measured with respect to Polyamides 1 to 5 produced above.

#### 4-3) Formation of Multi-Layer Structure

Using the Polyamide Resins 1 to 5 produced in the above section 4-1), the following multi-layer structures were formed.

##### 4-3-1) Fabrication of multi-layer sheet

The multi-layer sheets of Polyamides 1 to 5 were formed as follows. Namely, using a multi-layer sheet forming apparatus comprising four extruders, feed block, T die and take-up unit, Polyamide 1 to 5 for layer A, Polypropylene for layer B (available as "EC-9" from Nippon Polypro Co., Ltd.; MFR = 0.6), and Modified Polypropylene for adhesive layer of bonding the layers A and B (available as "Modick P-513V" from Mitsubishi Chemical Corp.) were made into a three-kind, five-layer sheet having a structure of layer B/adhesive layer/ layer A/ adhesive layer/layer B with the thickness of 360/20/40/20/360  $\mu\text{m}$ . The conditions, circumstances, and results for the above forming of multi-layer sheet are as follows.

(1) Polyamide 1; The extruding temperature of each resin in the sheet formation was 240 °C for the layers A and B and 220 °C for the adhesive layer, and the temperature of feed block was set up at 245°C. Malodor due to degradation of polypropylene during the extrusion was very slight. The width of multi-layer sheet obtained was 375 mm, and no defective appearance such as derived from irregular flowing of a flow-mark was seen. The thickness-distribution of each layer in the direction of the width was just as expected. Results for the thickness of each layer measured are shown in Table 1.

Table 1

	Distance from Center of Sheet (mm)						
	-150	-100	-50	0	50	100	150
Layer B+Adhesive							
Layer/ $\mu$ m	386	367	389	386	382	377	365
Layer A/ $\mu$ m	49	44	39	41	40	42	47
Layer B+Adhesive							
Layer/ $\mu$ m	343	376	364	361	343	365	341
Total/ $\mu$ m	778	787	792	788	765	784	753

(2) Polyamide 2; The excluding temperature of each resin in the sheet formation was 230 °C for the layer A, 240 °C for the layer B, and 220 °C for the adhesive layer. The temperature of feed block was set up at 235°C. Malodor due to degradation of polypropylene during the extrusion was very slight. The width of multi-layer sheet obtained was 375 mm, and no defective appearance such as derived from irregular flowing of a flow-mark was observed. In addition, the thickness-distribution of each layer in the direction of the width was just as expected. Results for the thickness of each layer measured are shown in Table 2.

Table 2

	Distance from Center of Sheet (mm)						
	-150	-100	-50	0	50	100	150
Layer B+Adhesive							
Layer/ $\mu$ m	348	358	398	384	381	371	356
Layer A/ $\mu$ m	56	49	42	40	43	46	52
Layer B+Adhesive							
Layer/ $\mu$ m	343	386	364	378	356	358	342
Total/ $\mu$ m	747	794	804	801	780	775	750

(3) Polyamide 3; The excluding temperature of each resin in the sheet formation was 260 °C for the layer A, 240 °C for the layer B, and 220 °C for the adhesive layer. The temperature

of feed block was set up at 255°C. Malodor due to degradation of polypropylene during the extrusion was emitted, and a white smoke was observed at the part where the resin was projected. The width of multi-layer sheet obtained was 375 mm, and no defective appearance such as derived from irregular flowing of a flow-mark was seen. In addition, the thickness-distribution of each layer in the direction of the width was just as expected. Results for the thickness of each layer measured are shown in Table 3.

Table 3

	<u>Distance from Center of Sheet (mm)</u>						
	-150	-100	-50	0	50	100	150
Layer B+Adhesive							
Layer/ $\mu$ m	358	369	385	389	383	377	352
Layer A/ $\mu$ m	72	56	48	40	42	48	65
Layer B+Adhesive							
Layer/ $\mu$ m	341	366	359	369	374	365	355
Total/ $\mu$ m	771	791	792	798	799	790	772

(4) Polyamide 4; The excluding temperature of each resin in the sheet formation was 230 °C for the layer A, 240 °C for the layer B, and 220 °C for the adhesive layer. The temperature of feed block was set up at 235°C. Malodor due to degradation of polypropylene during the extrusion was very slight. The width of multi-layer sheet obtained was 370 mm.

Flow-marks due to the irregular flow in the formation of the multi-layer sheet occurred, and the appearance was defective. In addition, the layer A resulted in being extremely thick at the edge of the sheet and in failure to obtain a sheet having a uniform thickness-distribution of layer A in the direction of the width. The thickness of each

layer measured are shown in Table 4.

Table 4

	Distance from Center of Sheet (mm)						
	-150	-100	-50	0	50	100	150
Layer B+Adhesive							
Layer/ $\mu$ m	335	366	358	379	375	367	341
Layer A/ $\mu$ m	136	97	68	42	43	102	154
Layer B+Adhesive							
Layer/ $\mu$ m	343	374	388	358	368	350	322
Total/ $\mu$ m	814	837	814	779	786	819	817

(5) Polyamide 5; The excluding temperatures of each resin in the sheet formation was 240°C for the layer A, 240 °C for the layer B, and 220 °C for the adhesive layer. The temperature of feed block was set up at 245°C. Malodor due to degradation of polypropylene during the extrusion was slight.

The width of multi-layer sheet obtained was 365 mm. Flow-marks due to the irregular flow in the formation of the multi-layer sheet occurred, and the appearance was defective.

In addition, the layer A resulted in being extremely thick at the edge of the sheet and in failure to obtain a sheet having a uniform thickness-distribution of layer A in the direction of the width. The thickness of each layer measured are shown in Table 5.

Table 5

	Distance from Center of Sheet (mm)						
	-150	-100	-50	0	50	100	150
Layer B+Adhesive							
Layer/ $\mu$ m	322	378	349	355	362	360	352
Layer A/ $\mu$ m	160	122	87	41	39	76	121
Layer B+Adhesive							
Layer/ $\mu$ m	324	339	381	380	364	371	331
Total/ $\mu$ m	806	839	817	776	765	807	804

#### 4-3-2) Fabrication of multi-layer container



Using a vacuum/pressure forming machine, the multi-layer sheets obtained in the above were fabricated into a cup-shaped container having a depth of 26 mm, an opening diameter of 64 mm, and a bottom diameter of 53 mm by a thermal deep drawing.

The thermal forming was conducted by heating the surface of the sheet to 170 °C using a ceramic heater up to 450 °C, and then immediately forming the sheet by a vacuum/pressure molding.

Results for the fabrication of the multi-layer containers are shown in the following:

Polyamide 1; The thermal formability into a container was very good, and a highly transparent container having a uniform thickness of the layer A was obtained.

Polyamide 2; The thermal formability into a container was very good, and a highly transparent container having a uniform thickness of the layer A was obtained.

Polyamide 3; At the time of the thermal forming into a container, elongation, defect, or partial whitening resulted from the crystallization of the layer A was seen, and the thickness of the intermediate layers was not uniform.

Polyamide 4; The thermal formability into a container was very good, but the thickness of the layer A was not uniform because the flow marks and the thickness-gap in the direction of width with respect to the multi-layer sheet were large, and the appearance was deteriorated.

Polyamide 5; The thermal formability into a container was very good, but the thickness of the layer A was not uniform because the flow marks and the thickness-gap in the direction of width

with respect to the multi-layer sheet were large, and the appearance was also deteriorated.

#### 4-4) Summarization

Summarization is shown in Table 6.

Table 6

Polyamide	1	2	3	4	5
	Ex. 2 of Present Invention	Ex. 3 of Present Invention	Comp. Ex. 1 of Present Invention	Ex. 3 of D1	Ex. 3 of D1
Composition IA/AA (mol%) Amine	6/94 MXDA	15/85 MXDA	0/100 MXDA	15/85 MXDA	7/93 MXDA
Relative viscosity	2.5	2.5	2.6	2.0	2.0
Melting Point (°C)	232	216	240	215	230
Half Cry- stallization Time (sec)	62	455	25	403	52
Oxygen Transmission Coefficient (cc. mm/ m <sup>2</sup> . day. atm)	0.07	0.07	0.09	0.08	0.07
Odor	None	<Formability of Multi-Layer Sheet> None Malodor due to Decomposition of PP			None
Appearance Thickness	Good Uniform	Good Uniform	Good Uniform	Bad Gap at Edge	Bad Gap at Edge
Thermal Formability	Good	Good	Bad	Good	Good
Appearance Thickness	Good Uniform	<Formability of Multi-Layer Container> Good Bad Uniform Not Uniform			Bad Not Uniform

5. Conclusion

As seen in Results of experiment, the polyamide resin of the present Application provides superior effect in both the formability of multi-layer sheet and the formability of multi-layer container, compared with the polyamide resin of Matlack reference (US Pat. 5,028,462) prepared by a polycondensation method without a solid-phase polymerization.

I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Tomomichi Kanda  
Tomomichi Kanda

Date: December 26 , 2005